Air quality impact for industrial area of Taranto city (South Italy): a multivariate statistical analysis application

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In order to assess the impact of industrial emissions on Taranto air quality, PM2,5 monitoring campaigns have been performed in the risk area of Taranto (via Orsini and via Dante sampling sites), during the months of October 2005 and February 2006. On the samples collected chemical characterization has been performed (ions, aromatic polycyclic hydrocarbons and carbon fraction). Even though via Orsini sampling site, located close to the industrial area, does not show PM2,5 concentration values different in comparison with the other sampling site, it shows higher concentrations of PAHs. Moreover during some days with specific weather conditions, it is possible to note high concentration values of micro-pollutants in the samples collected in via Dante sampling site, located in the downtown of Taranto city.
Principal Component Analysis (PCA) and Absolute Principal Component Scores (APCS) have been performed on the data obtained. Statistical analysis of PM components has highlighted an important contribution of industrial facilities on the air quality in Taranto city.

1. Introduction

Taranto (198.000 inhabitants) is a city placed in the heart of the Mediterraneo; it is the chief town of the homonymous province and the third more densely-populated town of the southern Italy. The city is placed in the middle of an area of 217 Km^2 characterized by high density of traffic associated to a productive model diffused in the territory.
The presence of a very wide industrial area close to the town and the numerous maritime and military activities in the harbour area constitute further factors of great interest which are worth attention. In fact, Taranto province has been defined as a “risk area” due to the numerous industrial activities of high impact present on the territory; moreover the province has been object of several initiatives with the intention of assessing and restoring very critical situations. Among the industrial activities particular attention is turned to the steelworks which represent one of the biggest steel manufacturer plants among Europe. The iron and steel Taranto pole is extended on a surface of 15.000.000 m^2 and inside it there are 200 Km of railway tracks, 50 Km of roads, 190 Km of conveyor belts, 5 blast furnaces and 5 converters. It is common knowledge that vehicular traffic and the industrial activities are among the main

anthropic particulate matter (PM2.5) sources. PM2.5 compounds and the presence of residual toxic substances of the combustion, make particulate matter very harmful pollutant for the human health and the environment.

2. Experimental methods

Two seasonal sampling campaigns were conducted between autumn 2005 and winter 2006 in Taranto (Puglia, south of Italy). The sampling sites were located in urban and industrial areas and were selected to compare an area characterized by high density of traffic and located in a main street (Via Dante) with an area close to the industrial area (Via Orsini).

Two low-volume particle samplers (FAI Instruments model Hydra Dual sampler) were used to collect ambient PM2.5. PM2.5 samples were collected on quartz fiber filters (Schleicher & Schuell, 47 mm diameter) by FAI EN 1234.1 sampling heads operating at a flow rate of $1m^3$/h or of $2.3m^3$/h. Daily samples were collected during October 2005 and between 31 January and 28 February 2006.

The quartz fiber filters were weighted, before and after the particulate sampling, with a Genius Sartorius SE2-F analytical microbalance with a sensibility of 0.0001 mg (Sartorius, Milan, Italy) provided with an ionizer for electrostatic charges abatement. The relative humidity and temperature in the weighing room were 44 ± 7 % and 22 ± 3 °C and the samples were stabilized in these conditions for 48 hours before weighing.

The filters were cut off into four pieces for the chemical analyses.

A quarter of PM2.5 samples was extracted by ultrasonic agitation for two 20 minutes steps using in all 10 ml of deionized water. Obtained solutions were analyzed for chloride (Cl^-), nitrate (NO_3^-), sulphate (SO_4^{2-}), sodium (Na^+), ammonium (NH_4^+), potassium (K^+), and calcium (Ca^{2+}) ions. Analyses were performed using a Dionex DX120 (Dionex, Sunnyvale, CA, USA) Ion Chromatography system for anions and a Dionex DX600 Ion Chromatography system for cations, equipped with an electrical conductivity detectors. An AS40 autosampler was used to analyse anions and cations simultaneously. Standard solutions were prepared by suitable dilution of their stock solutions (1000 mg/L from Fluka, Milwaukee, WI, USA) in Milli Q water. (Millipore Corporation, Billerica, MA, USA).

Rectangular punches (normally 1.50 cm^2) of filter deposit PM2.5 were analyzed for the detection of the organic and elemental carbon by a thermal optical method. To remove possible carbon contamination, quartz fiber filter were pre-cleaned in a muffle furnace (NIOSH METHOD 5040). In this method speciation of organic carbon (OC), carbonate (CO_3^{2-}) and elemental carbon (EC) is accomplished through temperature and atmosphere control. He-Ne laser light passed through the filter allows continuous monitoring of filter transmittance and an optical feature corrects for pirolitically generated OC. A flame ionization detector is used for quantification of evolved carbon and instrument calibration is achieved through injection of a known volume of methane into the sample oven (Birch and Cary, 1996).

The extraction of aromatic polycyclic hydrocarbons (PAHs) was realized by a microwave assisted solvent extraction (Milestone s.r.l. model Ethos D, Sorisole (BG), Italy). The extracted samples were analyzed using an Agilent 6890 PLUS gas

chromatograph (Agilent Technologies, Wilmington DE) equipped with a programmable temperature vaporization injection system (PTV) and interfaced to a mass selective spectrometer with an inert ion source (Agilent MS-5973 N) (Bruno et al., 2007a). The attention was focused on benzo[a]anthracene (BaA), benzo[b+j]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IP), benzo[g,h,i]perylene (BgP), and dibenzo[a,h]anthracene (DbA).

3. Results and Discussion

Figure 1 shows the daily mean PM2.5 samples collected in two monitoring site: via Orsini and via Dante. Two sites were characterized by high peaks of concentration during some sampling days of October and February.
Daily mean PAH concentrations, obtained analyzing PM2.5 samples, were calculated.

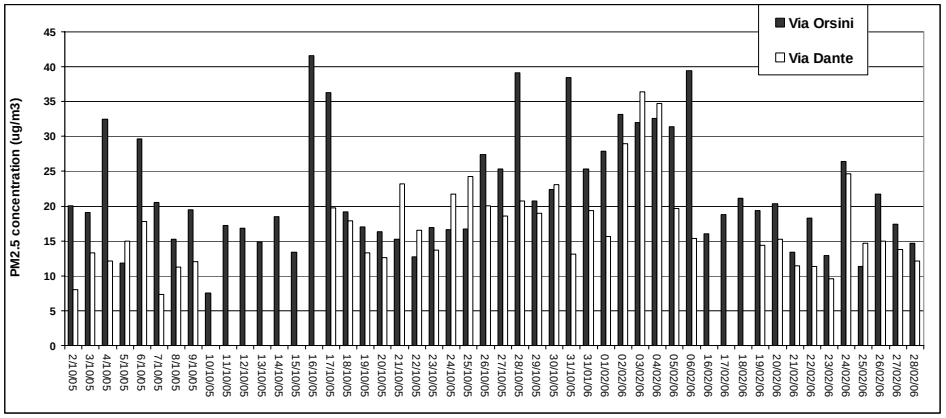

Fig.1*:* PM2.5 concentrations collected during the two monitoring campaigns in via Orsini and via Dante.

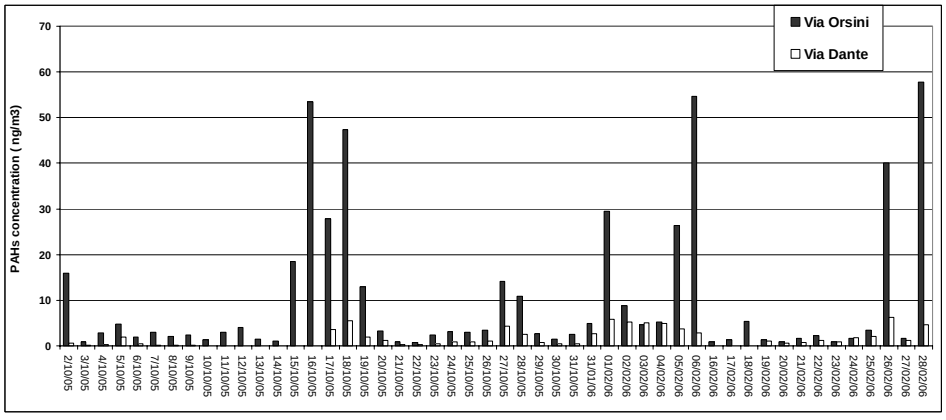

Fig.2: Daily mean concentrations of PAHs obtained analyzing PM2.5 samples collected in via Orsini and via Dante.

PAH ground level concentrations were similar in two sampling sites (Figure 2) except during the peak PAH episodes. During the days characterized by wind blowing from the industrial area (2, 15-18, 27-28 October and 1, 5-6, 26, 28 February) PAH concentrations in via Orsini reached to 58 ng/m^3 (Figure 3). When the wind was blowing from the north the emissions of the industrial area contributed also to the detected concentrations in the site of via Dante, in the urban area of Taranto. Even if PAH concentrations in via Dante were about 10 times lower than those of via Orsini, the trend of the concentrations during the sampling campaign was similar; the peaks of concentrations occurred during the same days in two sites.
High PAH levels were also detected during the days 5, 19 October and 2-4, 9-11 February that were characterized by calm wind conditions (Figure 3). Different studies (Sharan and Yadav, 1998; Goyal and Rama Krishna, 2002) showed that low wind conditions produce low dispersion capacity of the pollutants.

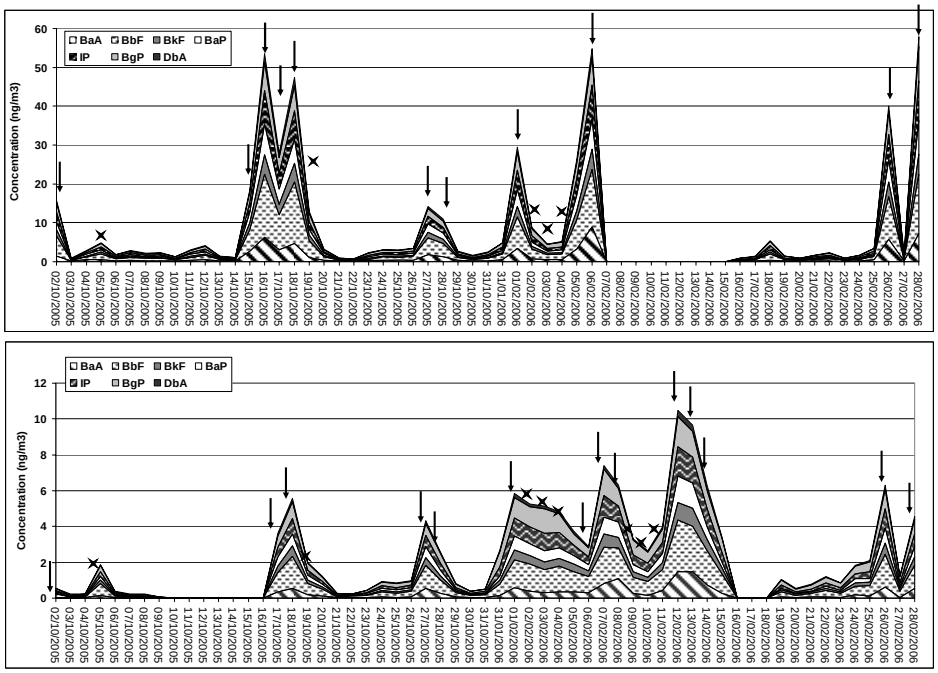

Fig.3: Trend of the investigated PAHs in two monitoring sites: up in via Orsini and down in via Dante. The arrows indicate the days characterized by wind blowing from north direction, while the stars show the days characterized by wind calm.

During these days the high concentrations of PAHs can be caused from the high levels of the previous day or produced by typical sources of the sampling site.
In the site of via Dante we can state that the high concentrations were due to the vehicular traffic, an important source of PAHs in the urban area of Taranto. Multivariate receptor models have become very popular in air pollution studies over the past decades (Manoli et al., 2002; Bruno et al., 2007b). Principal component analysis (PCA) and

Absolute Principal Component Scores (APCS) (Caselli et al., 2006) were applied on the data of chemical characterization of PM2,5 samples collected in via Orsini (Taranto city) monitoring station during the months of October 2005 and February 2006, in order to study in detail the characteristics of site.

PCA is a multivariate analysis technique used to reduce data dimensionality to a smaller set of orthogonal factors of easier interpretation (Vandeginste et al., 1998). Results obtained by PCA for the data set of the PM2.5 samples collected in via Orsini are shown in Table 1. Four principal components (PCs) together explain a large fraction (85,5%) of the total variance. The first component (PC1) could be considered as local primary emissions, probably due to anthropogenic and natural sources. This component is very important (explaining about 50% of the total variance), but it is very complex. In fact, although high loadings for PAHs, principally deriving from industrial and traffic emissions, are present, it can be also observed the association of PAHs with Cl^-, CO_3^{2-} and Na^+ (higher loadings), and with Ca^{2+}. K^+ and SO_4^{2-} (lower loadings). These parameters may have both marine and crustal, and industrial origin. The second component (PC2) could be attributed to secondary vehicular traffic emissions, deriving from gas to particle conversion processes by local nitrogen dioxides and volatile organic compounds oxidation. The third component (PC3) is due to regional NH_4^+ and SO_4^{2-} (secondary inorganic particulate). Finally, the fourth component (PC4) could be caused by primary vehicular traffic emissions, consisting in both exhaust emissions and resuspended road dust.

Table 1

Loadings, eigenvalues and percentage of variance explained obtained for each component in PCA applied to the PM2.5 samples of via Orsini. Only component loadings with absolute values greater than 0.2 are presented; component loadings with absolute values greater than 0.7 are presented in bold, component loadings with absolute values smaller than 0.7 in cursive grey.

Species	**PC1**	**PC2**	**PC3**	**PC4**	**PC5**	**PC6**
EC	-0,30	0,41	0,20	*-0,53*	*-0,56*	0,32
OC		**0,85**		-0,38		-0,23
Cl^-	**-0,72**		-0,35	0,42	-0,24	
CO_3^{2-}	**-0,91**				-0,23	-0,21
Ca^{2+}	*-0,67*		0,33		-0,47	-0,38
K^+	*-0,67*	0,30	-0,28	0,38		0,39
Na^+	**-0,89**		-0,25			
NO_3^-	-0,29	**0,79**	-0,44			
NH_4^+	-0,42	*0,63*	*0,52*	0,26	0,25	
SO_4^{2-}	*-0,65*		*0,67*			
BaP	**-0,93**	-0,27				
IP	**-0,92**	-0,27		-0,20		
BgP	**-0,92**	-0,25		-0,22		
BbF	**-0,92**	-0,27		-0,23		
Eigenvalues	7,2	2,3	1,4	1,1	0,9	0,6
% variance	51,6	16,6	9,7	7,6	6,3	3,9

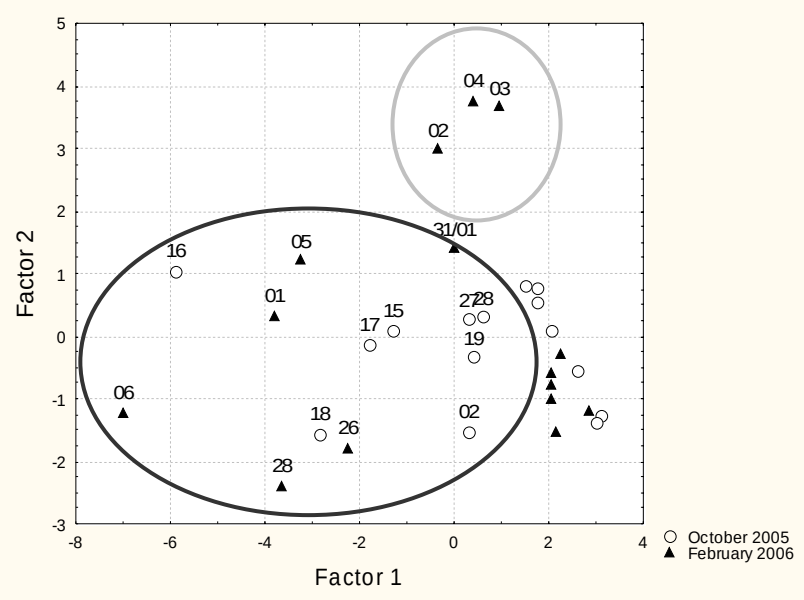

Fig. 4: Scatter plot of scores obtained for the components 1 and 2 in PCA applied to the PM2.5 samples of via Orsini.

Considering the scores plot in the plane of first and second CPs (figure 4), obtained for the PM2.5 samples of via Orsini, it is possible to note two types of events, highlighted in circular lines. The samples enclosed in the black circular line show high concentrations of PAHs, correspond to days of peak PAH episodes characterized by wind blowing from industrial area, shown in figure 3, while the samples contained in the grey circular line show higher values of nitrate and organic carbon, probably due to the low wind conditions, favoring secondary compounds production.

The APCS receptor model has been applied in order to identify the profile sources and their contributions. The results for PM2,5 samples collected in Taranto city showed the presence of recurrent sources, such as vehicular traffic, marine aerosol, secondary and crustal particulate matter. As one can see observing figure 5 EC is almost completely apportioned to vehicular traffic and resuspended source (the weight percentage of the source to the PM2,5 samples is 23%); OC is apportioned to source named "Organic carbon and nitrate" (which weight percentage to PM2,5 samples is 35%) and vehicular traffic source and resuspended; Cl^- to "sea and carbonate" source (which weight percentage to the PM2,5 samples is 8%) for the most part and to crustal source (which weight percentage to the PM2,5 samples is 9%); CO_3^{2-} is apportioned mostly to crustal source and "sea and carbonate" source; Ca^{2+} completely to crustal source; K^+ mostly to "sea and carbonate" source and for minor part to vehicular traffic and ammonium sulphate sources, that is secondary particulate (which weight percentage to the PM2,5 samples is 23%); Na^+ is mainly apportioned to "sea and carbonate" and traffic sources; NO_3^- to "organic carbon and nitrate" and "sea and carbonate" sources; NH_4^+ and SO_4^{2-} to ammonium sulphate source. Finally all four PAHs are mostly apportioned to Industrial and traffic source (which weight percentage to the PM2,5 samples is 2%).

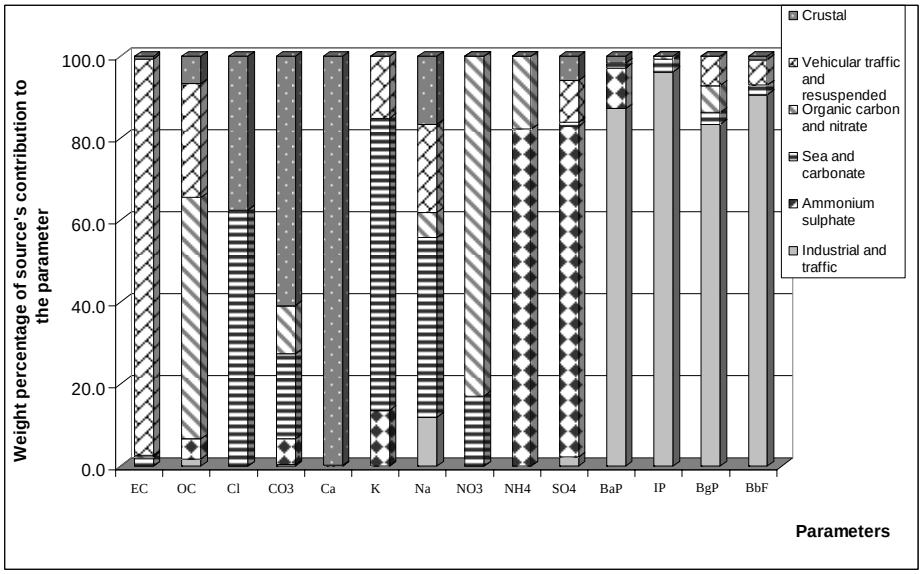

Fig. 5: the Y axis shows the weight percentage of each source's contribution to the parameter considered; X axis shows the parameters: elemental carbon (EC), organic carbon (OC), chloride (Cl), carbonate (CO3), calcium (Ca), potassium (K), sodium (Na), nitrate (NO3), ammonium (NH4), sulphate (SO4), Benzo[a]anthracene (BaP), Indeno[1,2,3-cd]pyrene (IP), Benzo[g,h,i]perylene (BgP), Benzo[b+j]fluoranthene (BbF).

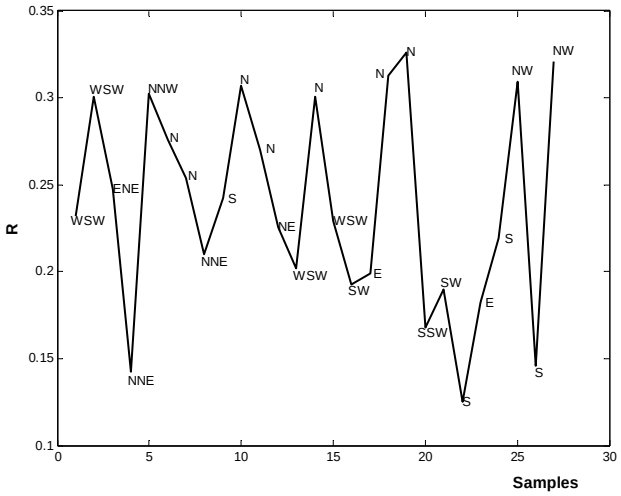

Fig. 6: R is the ratio between the contribute of Industrial source and the sum of the contributions of all three sources. The daily mean wind direction are shown.

It is important to note that even thought the weight percentage of the “Industrial and traffic” source is 2% only, all four PAHs considered are apportioned to this source for a percentage higher than 80%.
In figure 6 the ratio between the contribute of Industrial source and the sum of the contributions of all three sources (R) is shown. These sources have been obtained by applying the APCS method to the PAH data of the samples collected at via Orsini sampling site. As one can see the maximum value of R is obtained when the daily mean wind direction comes from North, that is when the air masses reach the sampling site coming from the industrial area of Taranto city. Although the contribution of industrial activities to the mass of PM2,5 is low, it affects largely to the concentrations of micro-pollutants such as PAHs, influencing the PM toxicity. Moreover this suggests mass of fine fractions of PM is not a good index of dangerousness of PM.

4. Conclusions

During this study it has been possible to point out the contribute of industrial area to the PM2,5 samples collected. This contribute is not evident in terms of PM2,5 weight, but in terms of concentrations of micro pollutants such as PAHs. This means mass of fine fractions of PM is not a good index of dangerousness of PM.

5. References

Birch M.E., A.M. Cary, 1996, Aerosol Science and Technology, vol. 25: Elemental Carbon-Based Method for Monitoring Occupational Exposures to Particulate Diesel Exhaust, Elsevier Science Inc.

Bruno, P., M. Caselli, G. de Gennaro, M. Tutino, 2007a, Determination of polycyclic aromatic hydrocarbons (PAHs) in particulate matter collected with low volume samplers, Talanta 72, 1357.

Bruno P., M. Caselli, G. de Gennaro, P. Ielpo, B.E. Daresta, P.R. Dambruoso, V. Paolillo, C.M. Placentino, L. Trizio, 2007b, Application of Receptor Models to Airborne Particulate Matter, Microchemical Journal doi:10.1016/j.microc.2007.11.018.

Caselli M., G. de Gennaro and P. Ielpo, 2006, A comparison between two receptor models to determine the source apportionment of atmospheric pollutants, Environmetrics 17, 1.

Goyal P. and T.V.B.P.S. Rama Krishna, 2002, Dispersion of pollutants in convective low wind a case study of Delhi, Atmospheric Environment 36, 2071.

Manoli, E., D. Voutsa, and C. Samara, 2002, Chemical characterization and source identification/apportionment of fine and coarse air particles in Thessaloniki, Greece, Atmospheric Environment 36 (6), 949.

Sharan, M. and A.K. Yadav, 1998, Simulation of diffusion experiments under light wind, stable conditions by a variable K-theory model, Atmospheric Environment 32, 3481.

Vandeginste, B.G.M., D.L. Massart, L.M.C. Buydens, S. De Jong, P.J. Lewi, J. Smeyers-Verbeke, 1998, Data handling in science and technology. Handbook of Chemometrics and Qualimetrics. Part B. Elsevier, Amsterdam.